Final Work plan

with

Quality Assurance Project Plan

for

Solid Phase Microextraction Sampling

at

Pacific Sound Resources Superfund Site

Seattle, WA

Prepared For:

Region 10
Seattle, WA

Prepared by:

Seattle District

March 12, 2018

Signature Page

EPA Region 10 Remedial Project Manager: Ravi Sanga — Date: 3/26/2018

EPA Region 10 Quality Assurance Manager: Donald Brown — Date: 3/22/2018

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USACE Project Manager: Amy Baker — Date

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USACE Technical Team Lead: Bill Gardiner — Date

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1.0 Project Management, Planning and Objectives

1.1 Problem Statement and Purpose

During the 1998 RI/FS for the Pacific Sound Resources (PSR) Superfund Site, dissolved-phase groundwater contamination and "fingers" of NAPL were found to extend from the Upland Unit containment wall area towards the Marine Sediments Unit in Puget Sound. Based on modeling conducted during the RI/FS, dissolved-phase contaminants associated with these NAPL fingers were not likely to impact sediment or surface water protectiveness. However, during subsequent monitoring, EPA noted both new NAPL detections and exceedances of cleanup goals in groundwater shoreline wells, indicating a potential risk of contaminated groundwater discharge through the placed sediment cap to surface water. A determination of whether dissolved-phase contaminants impact surface water quality at PSR is necessary to confirm both current and future remedy protectiveness. In short, it is currently unknown (a) whether dissolved-phase contaminants currently or will likely in the future impact surface water quality at PSR and (b) if potentially mobile NAPL detected beyond and below the slurry wall could reach the mudline.

The purpose of the work described in this field work plan is to collect porewater samples in areas of most-likely contaminated groundwater discharge to site sediment and surface water. The U.S. Environmental Protection Agency (USEPA) Region 10 has requested the Seattle District, U.S. Army Corps of Engineers (USACE) to plan for and deploy the vertical-profiling solid-phase microextraction (SPME) technology in order to determine the extent of creosote-related porewater contamination in the capping material and underlying sediment. This Work Plan describes the SPME field deployment required to quantify polycyclic aromatic hydrocarbons (PAHs) in PSR site sediment porewater.

Results will be used to determine if contaminated site groundwater is currently impacting sediment porewater and surface water quality in areas of most likely groundwater-to-surface water discharge pathways.

1.2 Project Organization, Responsibilities and Authority

Ravi Sanga	U.S. Environmental Protection Agency Region 10 1200 Sixth Ave., Suite 900 Seattle, WA 98101 206-553-4092 Sanga.Ravi@epa.gov	EPA Remedial Project Manager
Amy Baker	U.S. Army Corps of Engineers 735 E. Marginal Way S, Bldg 1202 Seattle, WA 98134-2385 206-764-3322 Amy.J.Baker@usace.army.mil	USACE Project Manager

Bill Gardiner	U.S. Army Corps of Engineers 735 E. Marginal Way S, Bldg 1202 Seattle, WA 98134-2385 206-764-3322 William.W.Gardiner@usace.army.mil	USACE Risk Assessor
Donald Brown	U.S. Environmental Protection Agency Region 10 1200 6th Avenue Suite 900 Seattle, WA 98101 206-553-0717 Brown.DonaldM@epa.gov	EPA QA Manager
Jacob Williams	U.S. Army Corps of Engineers 735 E. Marginal Way S, Bldg 1202 Seattle, WA 98134-2385 206-316-3157 Jacob.a.williams@usace.army.mil	USACE Chemist

1.3 Roles and Responsibilities

EPA Remedial Project Manager

The EPA Remedial Project Manager (RPM), Ravi Sanga, is responsible for providing direction to USACE and maintaining communication between all parties involved in the field sampling event. All final documents will be submitted through the RPM. He will also coordinate internally with EPA peers to facilitate review of this WP-QAPP and secure funding.

EPA QA Manager

The EPA QA manager, Donald Brown, will serve as the EPA quality assurance manager for this project. He will review this WP-QAPP and be available to answer questions regarding data validation and usability for this project.

USACE Project Manager

The project manager (PM), Amy Baker, is responsible for the execution of the scope, schedule, and budget for the PSR sampling on behalf of EPA. She is the primary POC for communications with EPA. The USACE PM will oversee all activities of the USACE project delivery team (PDT), including quality assurance reviews, and maintain regular coordination (update email/calls; scheduled meetings at least quarterly) with the EPA to ensure adequate and timely flow of information for all work required under this agreement. The USACE PM also has the authority stop work of USACE staff.

USACE Technical Lead

Bill Gardiner is the designated technical lead for this project. He is responsible for coordinating the sampling event, and is also the field sampling lead. He will ensure the execution of sampling, and shipping of samples to the project laboratories. He also leads the readiness review meeting before the sampling event to ensure that field personnel are familiar with and adhere to proper

sampling procedures, field measurement techniques, sample identification, and chain-of-custody (CoC) procedures.

USACE Project Chemist

The project chemist, Jacob Williams, is the primary author for writing this WP-QAPP. He is directly responsible for any matters related to chemistry for this project. He shall be responsible for providing additional guidance to the field sampling team in any matters relating to project chemistry and data quality. He will also review analytical data as they become available to ensure conformance with quality standards, identify quality problems and verify corrective actions, ensure that electronic data are accurate and complete, and serve as a point of contact for issues related to environmental chemistry. He will also receive any data reviews performed by the lab and subsequent electronic data deliverables (EDDs).

Special Training Requirements and Certifications

Project staff shall be qualified to perform their assigned jobs. Field sampling personnel conducting or monitoring sampling activities are to be trained by the field sampling lead in accordance with established USACE protocols.

Field Staff

All project staff participating in on-site field activities shall have current HAZWOPER training in accordance with 29 Code of Federal Regulations (CFR) Part 1910.120.

Laboratory Contact

The analytical laboratories and applicable information that will be used for this project are listed below in Section 1.4.

1.4 Laboratory Contact

Laboratory	Shipping Address	Contact Information
Department of Civil, Environmental and Construction Engineering Texas Tech University	Texas Tech University Department of Civil, Environmental and Construction Engineering Texas Tech University 911 Boston Lubbock, Texas 7409-1023	**Danny Reible**, Principal Investigator danny.reible@ttu.edu (806) 834-8050
Analytical Resources Inc	Analytical Resources Inc. 4611 S 134th Pl #100 Tukwila, WA 98168	**Kelly Bottem**, Client Services manager kellyb@arilabs.com 206-695-6211

1.5 Project Schedule

Deliverable	Due	Comments
Planning and Update Meetings	As needed.	
WP-QAPP		
Draft WP-QAPP submitted	February 2018	MS Word (PDF as needed)
Final WP-QAPP submitted	March 2018	MS Word (PDF as needed)
Field Sampling		
Porewater/Sediment sampling	March 2018	
USACE/EPA review of analytical data.	Spring 2018, as data becomes available	
Report for Sampling Event		
Draft Final Report - includes field reports, sample shipment records, analytical results and QA/QC reports. Groundwater direction will be described, and recommendations made, if applicable.	Summer 2018	Electronic MS Word
Final Report	After receipt and incorporation of EPA comments on draft	Electronic MS Word, PDF upon request

2.0 Work Plan for Porewater Sampling at PSR using SPMEs

2.1 Technology Description

SPMEs consist of a sorbent polymer layer (polydimethylsiloxane or PDMS) of approximately 10 to 30 μm in thickness surrounding a glass core with thickness of 100-1000 μm (the smallest fibers are similar to the thickness of a human hair). The SPMEs are typically deployed directly into sediment inside perforated stainless steel PushPoint sampling devices (Figure 1). Rapid uptake of PAHs in the fiber occurs without interference of colloidally-bound contaminants, and this provides an improved measure of dissolved contaminant concentrations in porewater. Porewater provides a direct measure of bioavailable contaminants in sediment, and indicates the potential exposure for benthos and pelagic organisms.

Deployed SPMEs would be allowed to equilibrate with sediment porewater for 14 days before retrieval, which is a suitable period of equilibration time as determined by experience with comparable projects. Upon retrieval, the SPME fibers are cut into sections, extracted, and analyzed. The resulting SPME concentrations are converted to corresponding porewater concentrations using the regression relationships developed and reported in the SPME Calibration Study Report (2018 PSR Quality Assurance Project Plan (QAPP), Appendix A). Porewater concentrations are then compared to surface water ARARs for PAHs as shown in Table 4. Porewater concentrations will also be used to estimate corresponding sediment concentrations using equilibrium partitioning equations.

2.2 Data Quality Objectives

Data gaps, project objectives and investigation methods are summarized in Table 1 below. Referenced concentration ranges and analytical sensitivities for SPME porewater analysis are summarized in Table 4 of the QAPP. As described in the table below, co-located sediment grab samples will be collected during the SPME retrieval and will be submitted to the laboratory for analysis of PAHs and total organic carbon (TOC). While data quality objectives for the sediment samples are described here, detailed laboratory analysis requirements for PAHs and TOC will be conducted by a separate laboratory and will be described in an addendum to this work plan. Additional sediment sample volume will also be archived should analysis of other sediment COCs (PCBs, PCP, metals) be desired as well. Methods for sediment grab sample collection, handling and archiving are provided in Section 2.3.

Table 1. Data Quality Objectives

Data Gap	Project Objectives	Investigation Methods	Performance Goal	Decision Criteria
Is Elliott Bay sediment porewater currently contaminated with PAHs due to contaminated groundwater discharge from PSR Superfund Site?	Measure sediment porewater concentrations of PAHs directly downgradient of shallow groundwater discharge from areas where > 1 ft of NAPL staining was observed beyond the slurry wall during the RI/FS (RETEC 1998).	Insert SPME fibers up to 3 ft below the sediment surface and allow for equilibration with sediment porewater for 14 days. Retrieve SPMEs and section into discreet sample depth intervals (in the 0-4, 4-8, 20-24 and 30-34 inches below sediment surface intervals), preserve sections immediately in acetonitrile, and submit all samples for analysis of PAHs.	Detection limits for PAHs at or below surface water quality standards or as otherwise indicated in Table 4 of the QAPP.	Compare measured PAHs concentrations in the 0-4 and 4-8 inch SPME sections to surface water quality standards to assess compliance with ARARs and current impacts to near-surface sediment porewater. Results of deeper porewater sections (20-24") may indicate future cap contamination. If deeper contamination is detected, seepage velocity values may be used to calculate contaminant flux and time to potential contaminant breakthrough.
Do surface sediment concentrations of PAHs, in the vicinity of the proposed porewater sampling locations meet SQS criteria? Sediment PAH monitoring was not conducted in the SPME deployment areas during the 2007 Long-Term Monitoring Event due to a presumption that the capping material in these areas was clean.	Measure PAHs in surface sediments co-located with SPME deployment locations to determine compliance with SQS criteria.	Collect co-located surface sediment grab samples and place in 8 oz. glass jars. Submit for analysis of sediment PAHs and total organic carbon. Total organic carbon is a required input parameter for calculating porewater/sediment equilibrium partitioning values. All sediment samples will be archived pending SPME porewater results, which will be used as a basis to select subset of sediment samples to submit for analysis of PAHs.	Detection limits for PAHs at or below SQS standards or as otherwise indicated in Table 4 of the QAPP.	Compare measured concentrations of PAHs in sediment to SQS criteria to determine whether current conditions meet cleanup requirements. Sediment PAH concentrations will also be used to determine whether chemical equilibrium exists between sediment and porewater concentrations.

2.3 Field Deployment Methods

2.3.1 SAMPLING LOCATIONS

SPMEs will be deployed in twenty-five locations as indicated on Figure 2 and Table 5. The sample locations for the 2018 SPME sampling are the same as the 2011 sampling event, with the addition of one sample location (PSR-25). This new sample location extends the range in sampling by providing a new location in the south-western corner of the sampling area.

The western array (west of the point) is located downgradient from upland groundwater monitoring wells MW-5 and MW-14 series, which contain NAPL or elevated concentrations of PAHs (RETEC 2005). Samples in the eastern array are located down gradient of known NAPL impacted areas beyond the slurry wall containment area and downgradient from monitoring well MW-15IR, which was observed to contain NAPL during a September 2008 sampling round (USACE 2009). In addition, two SPMEs will be deployed to measure PAH concentrations in the water column. Water column SPMEs will be attached to the top of a stainless-steel push-point sampler, which will be inserted into the sediment so that the SPME fiber is suspended approximately 3 ft. above the sediment surface in the water column. Water column SPMEs will be located between SPME locations PSR 10 and PSR 4 in the western array and between PSR 17 and PSR 22 in the eastern array (Figure 2) and will remain deployed for the duration of the field test (14 days) to ascertain if any porewater PAH exceedances detected in SPMEs are reflected in the water column. An additional regional background and upgradient SPME water column sample location was selected in West Seattle where there are no known nearby sources of PAHs. The background water column sample will also be suspended approximately 3 ft. off the sediment bottom and will be located ~ 100 ft from the pilings of the nearby condominium building (Figure 3). The background surface water sample will be linked with cord to a select piling beneath the condo so that the divers may follow the cord to easily relocate the background sample during retrieval. This sample will be deployed and retrieved on the same day as all other samples.

Surface sediment samples will be collected at each SPME sampling location (following SPME retrieval) at a radial distance of 1 ft. from the SPME insertion location.

2.3.2 INSERTION TOOL PREPARATION

Before deployment, all SPME sampling devices (i.e. the insertion tool) will be cleaned with Alconox detergent and distilled water, then subsequently rinsed with hexane, acetonitrile and distilled water. The insertion tool should then be subjected to a final distilled water rinse. Once cleaned the components of the insertion tool are packaged together, inner and outer sheath and placed aside for installation of SPME fiber.

SPME fiber should be cleaned before being inserted into the insertion tool with high purity solvents that will be used to extract contaminants for post-retrieval chemical analysis (i.e. acetonitrile). Cleaning the fiber consists of rinsing sequentially in hexane, acetonitrile, and methylene chloride for 30 minutes, twice. Prior to placing the SPME fiber in the PushPoint sampler, the fibers will be soaked in performance reference compounds (PRCs). The PRCs are used to assess the kinetic dissipation/uptake rates during field deployments. The PRCs are deuterated/C^{13} labeled versions of the analytes of interest at working concentration of 2500 ng/ml in solvent. The acetonitrile is

disposed of and the fibers are rinsed with distilled water and a clean wipe. The rinse with distilled water will help to remove any acetonitrile residuals left on the fiber but any remaining residuals will quickly evaporate from the fiber. The stainless-steel tubing in which exposed samples will be returned to the laboratory should be cleaned in a similar manner.

The cleaned fiber is laid into a groove cut into the inner rod of the insertion tool using tweezers (see Figure 4). Silicon serves to hold the fiber in place and can also be used to fill any gaps at the ends of the insertion tool to eliminate any water movement vertically. Care should be taken to avoid any placement of silicon on the screened length or active measurement portion of the insertion tool or to place so much silicon that cured silicon will hinder insertion tool separation after field exposure. To make sure the fiber is securely in place, a finger should be run along the groove. In addition, the grooved rod can be held vertically to check for any SPME fiber movement. If the fiber moves during either test, the process of installing the fiber should be repeated.

Once it is clear the fiber is securely in place, the inner and outer rods of the insertion tool should be placed side by side to determine the point on the outer rod which marks the top of the fiber and mark this with a wrapping of waterproof electrical tape. The inner rod with the fiber is then inserted into the outer sheath with groove and fiber aligned with the screened side of the sheath. The handles on both inner grooved rod and sheath are then wrapped together so the two sets of handles will not twist relative to each other causing the SPME fiber to become misaligned with the screened section of the outer sheath. The length of fiber that was loaded into each of the insertion tools should be documented.

2.3.3 NUMBERING

When inner rod and sheath are assembled, forming the complete SPME loaded insertion tool, handles are wrapped with electrical tape and a numbering system is constructed to keep a record of which rod was placed in what location. Different color tape can help aid with identifying planned location of deployment. Each completed insertion tool is numbered on the taped portion of the handles and planned deployment location documented. Full insertion rod sample numbering will be as follows; see Table 2 for example sample designators.

ss-dddd-ll-xxy

sss – site (Pacific Sound Resources, PSR)

dddd – date (e.g. 061208 for June 12, 2008 deployment date

ll- location (e.g. CS for control sediment, SW for surface water)

xx- sample number (e.g. 1, 2…)

y – duplicate designator (a or b)

Table 2. Example sample designators.

Sample Designator	Matrix	Description	Analyses
PSR-092210-1-1a	SPME	Primary sample, location 1, within 0-4" depth (3-5 cm designated as sample a, 5-7 cm field duplicate designated as sample b)	PAHs
PSR-092210-1-2a	SPME	Primary sample, location 1, within 4-8" depth (13-15 cm designated as sample a, 15-17 cm field duplicate designated as sample b)	"
PSR-092210-1-3a	SPME	Primary sample, location 1, within 20-24" depth (54-56 cm designated as sample a, 56-58 cm field duplicate designated as sample b)	"
PSR-092210-1-4a	SPME	Archive sample, within 32-36" interval or otherwise the 4" interval from the greatest depth below the 24" sample where possible. (84-86 cm designated as sample a, 86-88 cm field duplicate designated as sample b)	"
PSR-092210-BKGDSW-1	SPME	Sample deployed in the water column ~ 3 ft above the sediment surface near Alki Beach in area free of known creosote sources and upgradient of PSR site based on surface water circulation patterns in Elliott Bay.	"
SW-1	SPME	Sample deployed in the water column ~ 3 ft above the sediment surface in the western cluster of SPME locations at PSR.	"
SW-2	SPME	Sampler placed approximately 3 feet above the seafloor by inverting a PushPoint sampler.	"
PSR-092210-1	Sediment	Co-located surface sediment grab samples will be collected following SPME insertion at each location. The sediment grab will be collected from a distance of ~ 1ft from the SPME insertion location so as not to disturb the inserted SPME.	Archive at -20°C

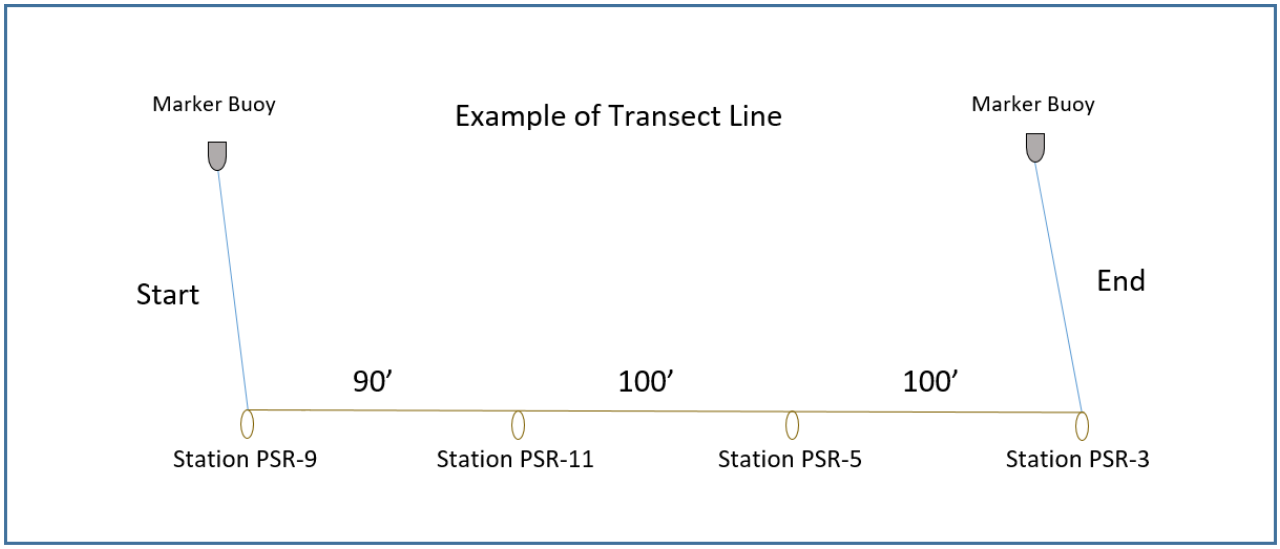
2.3.4 DEPLOYMENT

Once received at the desired location, all SPME insertion tools are deployed. The insertion tools are inserted to the point marked on the outer sheath where the top of the fiber is within the device. Insertion tools are inserted perpendicular into the sediment so a profile can be achieved. The PushPoint sampler provided from the laboratory will include 30, 42" insertion tools with a 36" sampling section. The insertion tool will attempt to be submerged the complete 36'' into the sediment. If there is refusal inserted the tool to this depth, it will be submerged as deep as possible and the insertion depth recorded. The 36" working length will be used to sample the regions 0-10 cm (0-4"), 10-20 cm (4-8"), and 51-61 cm (20-24") and 76-86 cm (30-34") below the sediment surface. SPME Samplers will be given to and deployed by EPA divers. All insertion tools will be connected with zip ties via nylon cording. The location of the cording will be marked at the surface with submerged crab pot buoys.

SPME samplers will be deployed at 25 stations. 24 stations are placed on seven transects of three or four stations. One station will be located by coordinates without a transect line. The transects and corresponding stations are listed in Table 1. The coordinates for the 25 stations are listed in Table 4.

Prior to the field event, transect lines will be created for each transect, with the stations marked on each transect line. The transect line will be premeasured and precut, with the distances between each station measured from the start point. For example, the line for Transect #1 will be 290 ft. long. The start point will be marked for Station 9; then 90 ft of line will be measured out and

Station 11 marked. An additional 100 ft of line is then measured out and Station 5 marked; followed by an additional 100 ft. of line to the end point, where Station 3 is marked. To support sampler retrieval, a loop should be tied at each station location. The insertion tool can then be placed through the loop as it is inserted into the sediment.



In the field, the boat in the field will then locate via GPS the end point of the transect. The End Point of the transect line will be anchored and marked with a buoy. The boat will then travel to the start location, paying out the transect line. Once at the Start Point coordinates, the transect line will be anchored and marked with a buoy.

The divers will be fitted with the appropriate SPME sample insertion tools, and descend the start anchor line. The divers will then move along the transect line, deploying the SPME samplers at the specified sample locations, and ascend at the end location which is marked with the anchored buoy. Notes on any surface features will be noted for each location, including substrate type, the presence of any vegetation, biota, or organic debris.

Sample location PSR-25 will be located on the boat, via dGPS, and marked for the divers to deploy at as an individual sample location. Due to its location, it is not part of a complete transect with any other samples. However, this sample will be connected via a tag line to transect #1. See Table 4 for the specific methodology of this deployment method, including the sample points of each transect, GPS coordinates of the start and end of each transect and the number of feet between each point within a transect. After all of the SPME samplers have been deployed, the transect lines while be left in place while the samplers equilibrate for 14 days, with submerged buoys also in place.

2.3.5 RETRIEVAL

This paragraph describes the standard operating procedure for retrieving a SPME fiber. During retrieval, the SPME fibers are withdrawn from the sediment and brought to the surface and immediately processed on the Wooldive boat. Field notes and pictures will be collected to document all variances from expected or design conditions as well as to confirm locations of the

field deployable SPME insertion tools and sample ID. The divers will also perform the work while wearing a "GoPro," which will film the process of SPME deployment and retrieval. Any staining or sediment present on the insertion tools should be noted.

Sectioning and processing of the SPME fibers will be conducted on the Wooldive boat by TTU staff. See Section 2.4.1 for processing methods. Sectioned samples will be shipped to the Texas Tech University (Texas Tech) for analysis. Field blanks will be processed identically as the samples as described in Section 2.4.1.

Sediment samples will be collected upon retrieval of the SPME at each sampling location. The samples will be collected by EPA divers at a distance of within 1 ft from the inserted SPME. The divers will collect surface sediment samples using a clean (foil wrapped) stainless steel spoon at each location. Surface sediment sampling depth will not exceed 10 cm below the sediment surface. Collected sediments will be placed into two 8 oz. glass jars filled with DI water beforehand, free of any air, so as to be neutrally buoyant during the dive and the lids will not be closed tightly to allow for easy opening by divers at depth. Lids for all jars will be pre-labeled. The EPA divers will then provide the filled sediment jars to the sample processing crew for labeling and storage at 4°C pending delivery to the laboratory at the end of each field day for storage at -20°C. The sample preparation crew will pour off excess liquid and provide some headspace in the jars to allow for sample expansion when frozen. The sediment samples will be handled under standard chain of custody procedures. Pictures will be taken throughout the process for documentation purposes.

2.3.6 ANALYTES, CONTAINERS, QUANTITIES, VOLUMES, PRESERVATION, AND HOLDING TIMES FOR SAMPLING

Table 3. Method Analysis Information and Quantities

Analytes	Media	Lab	Methods	Container type/quantity	Preservation	Holding Time	Number of field samples
PAH	Porewater	Texas Tech	EPA method 8310; SW-846	15 mL vial	Temperature: 4°C +/- 2°C, acetonitrile	14 days	150 (with 25 SPME samplers)
PAH and TOC	Sediment	Analytical Resources Inc.	EPA method 8310; SW-846 and EPA 5310b	8 oz glass jar	Temperature: 4°C +/- 2°C	14 days	25

Analytical Resources Inc. (ARI) will be analyzing the sediment samples. 5 sediment samples will initially be submitted for analysis at predetermined locations by EPA and USACE. The remaining 20 grab samples will be archived pending further decision making, after the results from the SPME fibers become available. This allows for time to review the results of the SPMEs and time for decision making to decide which additional sediment samples and analytes are desired for analysis.

2.3.7 DECONTAMINATION PROCEDURES

There will be individual insertion tools for each sample location used to deploy the SPME fibers, and each insertion tool will be rinsed and cleaned with Alconox detergent and distilled water, then subsequently rinsed with hexane, acetonitrile and distilled water, before it is deployed. When the SPME samples are retrieved, the insertion tool will be rinsed with DI water to remove any stains or sediment still on the tool.

During sediment sampling, a new, unused jar will be used for each sediment sample. A new spoon will be used between each sediment sampling location to prevent cross contamination of sediment samples.

The divers will be rinsed with potable water as they exit the water as a precautionary to remove any potential sediment, dirt or contaminants.

2.3.8 FIELD DOCUMENATION PROCEDURES

Field documentation provides a permanent record of field activities and can be used, if necessary, to trace possible introduction of field sampling error. Observations and measurements taken in the field will be recorded in field logbooks.

All field notes will be maintained in a numbered, bound logbook, which is assigned to a specific person who is responsible for entry of information into the logbook. All information pertinent to the sampling effort will be recorded in a field logbook. The Field Sampling Lead has overall responsibility for accuracy and completeness of field logbooks. Each page/form will be consecutively numbered. All entries will be made in indelible ink and all corrections will consist of lined-out deletions that are initialed and dated by the person making the corrections. Each page of the logbook should be signed and dated by the personnel responsible for observations. As a minimum, the applicable items for the entry into the logbook are listed below.

General Information

- Date
- Start and finish times of work
- Weather conditions
- Name and signature of person making entry
- Names of personnel present
- Names of visitors

Sampling Information

- Date and time of sample
- Photograph identification
- Location of sample (sample port or faucet)
- Type of sample
- Sample identification number
- Associated QC samples
- Flow rate
- Purge time
- Any unusual observations

The original field notes will be scanned and submitted as part of the final report. Records will contain sufficient information so that someone could reconstruct the sampling activity without relying on the collector's memory. The USACE Field Sampling Lead will keep a master list of all field logbooks assigned to the sampling personnel. The field sampling lead will review all daily entries in the field logbooks.

Photographs

Digital photographs will be taken to document sample locations. The subject of each photograph is the sampling location, the collection activity, and the associated sample jars. Digital photographs will be provided electronically to the USACE PM with the associated field logbook information. Information about each photograph will be recorded in the field logbook. The information will include:

- Date and time
- Compass direction
- Weather conditions (if applicable)
- Subject
- Purpose for photograph being taken
- Number of photograph
- Name of person taking photograph.

2.4 Field Sample Processing Methods Following Retrieval

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT (The Field Lead has ultimate responsibility for performing quality control checks on all the steps below)
Sample Collection (Personnel/Organization): The field lead agency (USACE) is responsible for implementing the SOP for sampling.
Sample Packaging (Personnel/Organization): Performed by USACE Field Team.
Coordination of Shipment (Personnel/Organization): Performed by USACE Field Team.
Type of Shipment/Carrier: Federal Express for Overnight Delivery
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Assigned lab personnel
Sample Custody and Storage (Personnel/Organization): Assigned lab personnel
Sample Preparation (Personnel/Organization): Assigned lab personnel
Sample Determinative Analysis (Personnel/Organization): Assigned lab personnel
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): Samples will not be stored in the field, but will be shipped within 24 hours of collection. If in an emergency they are stored in the field they will be kept in a cooler kept at 4±2 degrees Celsius.
SAMPLE DISPOSAL
Personnel/Organization: Assigned Lab Sample Custodians
Number of Days from Analysis: At least 60 days

2.4.1 SPME PROCESSING AND ANALYSIS

Insertion tools will be disassembled and SPME fibers will be processed by TTU staff in the field. The insertion tools are dismantled and the fibers are extracted from the inner rod. Any observations should be noted including color changes that may be due to changes in sediment biogeochemistry or evidence of relative rotation of the inner support rod or sheath should be documented. Samples should be handled with care when extracting the fiber from the inner rod since the sediment particles will most likely be packed into the inner rod and the fiber may be difficult to extract. After removing the tape from the handles, the inner rod should be carefully and slowly removed and placed on a flat surface with the grooved side facing upwards. The SPME fiber should be located and carefully removed and placed on a clean, high contrast surface with position of the sediment-water interface noted. If the fiber is broken during removal care should be taken to maintain relative position of the pieces. Any missing pieces or length, if any, should be documented and the overall length of fiber recovered documented. The fiber should be gently wiped with a clean tissue and distilled water to remove any sediment particles.

The fiber will be sectioned in the field into intervals corresponding to 0-4, 4-8, 20-24 and 30-34 inches below the sediment surface (0-10, 10-20, 51-61 and 76-86 cm, respectively) and 2 cm segments will be collected from within each of these SPME intervals. That is, from each 4 inch segment, the top 3-5 cm and 5-7 cm sections will be collected and immediately placed in separate vials containing 200 µL of acetonitrile to preserve and extract the samples. The 3-5 cm section within each depth interval will serve as the primary sample and the 5-7 cm section within each interval will serve as the field duplicate sample. This sectioning plan will result in a total of 4 primary samples and 4 field duplicate samples being collected at each SPME insertion location. The 30-34 inch fiber depth interval will be collected where SPME insertion depth allows..

For fiber cutting and analysis the following tools will be needed: small tweezers, single edged razor blade or capillary column cutter, 100 µL micro pipette, ruler with cm increments, Kim-wipes, distilled water, 2 mL autosampling vials with glass inserts prefilled with 200 µL of acetonitrile, sampling vial caps, and rack to hold sampling vials. All tools should be cleaned, and solvent rinsed before using.

Vials should be labeled prior to fiber cutting with any preferred method as per the method described above at a minimum including location, sample number and duplicate indicator. The fiber should be cut into sections depending on the detection abilities of the instruments being used for analysis and the concentrations expected. For the 30 µm PDMS fibers with 1 mm glass core to be used in this study, a 2 cm length of fiber is expected for each analysis. Cutting should begin at the top and continue to the bottom.

The cut fibers should be placed in the autosampling vial with insert and a syringe needle used to push the fiber to the bottom of the vial if the small fiber is used such that when solvent is added, the entire fiber will be immersed. 210 µL of acetonitrile will be prefilled into the sample vial to preserve and extract contaminants from the fiber. Testing has shown that extraction is essentially complete with gentle shaking of the vial after solvent addition for 30 seconds.

Solvent blanks (sample containers with acetonitrile but no SPME fiber) will be included to verify that there are no contamination issues prior to use. In addition, five calibration standards will be

shipped with the sampling vials, treated the same way as the field samples, and analyzed to indicate the solvent loss or possible contamination during shipping and handling. Internal standards maybe added to each sample vial depending on the feasibility. The current internal standards used by the laboratory are the 4 d-PAHs..

The sample can then be shipped to the Texas Tech lab and analyzed. During analysis the vial is placed in an autosampler. PAHs at Texas Tech will be analyzed with a high-performance liquid chromatography (Waters 2690 HPLC) with UV-Diode array detector and fluorescence detector will be used to measure the concentration of the extract. (EPA method 8310; SW-846 3rd edition, 1986). All 16 PAH priority pollutants, dibenzofuran, and 2-methylnaphalene will be analyzed using HPLC (acenapthylene is not detectable by fluorescent detection and higher detection limits than other compounds may be noted using UV detection (see calibration study, Reible 2010). In addition Benzo(g,h,i) perylene and Indeno(1,2,3-cd) pyrene are expected to coelute.

2.4.2 CUSTODY AND SHIPMENT

For shipping, the SPME rods Insertion tools should be loaded with SPME and constructed and shipped immediately before deployment to avoid potential sorption due to exposure to environmental contaminants. One SPME insertion tool should be prepared and shipped to the site but held back from deployment to serve as a field blank to identify possible contamination during shipping for placement. An additional blank will be deployed upon retrieval.

Processed SPME samples will be shipped under proper chain of custody operations to the laboratory in plastic coolers with packing materials. This includes all samples being labeled with its own sample ID, packaging samples in bubble wrap and securing them in iced coolers wrapped in tape, with the chain of custody in the cooler, for shipment. The SPMEs will be shipped under chain of custody procedures without refrigeration as samples will be preserved in acetonitrile immediately following collection.

2.4.3 DISPOSAL OF INVESTIGATIVE DERIVED WASTES

Personal protective equipment (PPE) for the sampling (consisting of Nitrile gloves) and other disposables used during sample preparation will be packaged in plastic garbage bags and disposed in a solid waste bin. All samples and chemical preservatives will be disposed of as per Texas Tech University hazardous material handling requirements.

3.0 Analytical Methods and Quality Assurance Requirements

The analytical procedures to be used for fixed laboratory analyses are described in this section. The analytical methods and associated quality assurance/quality control (QA/QC) procedures were selected based on consideration of the project objectives. The analytical methods, calibration procedures, and QC measurements and criteria are based on current analytical protocols in the following:

- EPA SW-846 *Test Methods for Evaluation of Solid Waste,* in particular Method 3510 or 3520 (extraction) and 8310 (High Performance Liquid Chromatography)
- Department of Defense Quality Services Manual
- Laboratory-specific standard operating procedures (SOP)

The methods selected will be sufficient to meet the project objectives. Laboratory QA will be implemented and maintained as described in this plan and according to the laboratories' QA plans and SOPs. While a best effort will be made to achieve the project performance goals, there may be cases in which it is not possible to meet the specified goals. Any limitation in data quality due to analytical problems (e.g., elevated detection limits) will be identified to the attention of the USACE Technical Team Lead. In addition, this information will be discussed in the data evaluation report.

3.1 Laboratory Analytical Methods, Method Detection, Quantitation and Reporting Limits

The analytical methods to be used by the laboratories are described in this section. The analytical methods and associated quality assurance/quality control procedures were selected based on consideration of the project objectives. Note that 15 of the 20 co-located sediment samples collected by EPA divers will be archived for analysis of PAHs and other sediment COCs in the future, pending results from the SPMEs and further decision making. Analytical requirements for the archived sediment samples will be addressed under a separate document.

SPMEs: Method (SW-8310): High-Performance Liquid Chromatography (HPLC) with a Fluorescence Detector FD. All samples will be analyzed by ultraviolet and fluorescent detectors although depending upon sample concentration only one will generally be used to quantify samplers (fluorescent for low concentration range samples, UV for high concentration range samples) Appendix B includes a table of method detection and practical quantitation limits for SPME analysis of PAHs, dibenzofuran, and 2-methylnaphalene.

Sensitivity requirements for all methods and matrices are driven by the intended comparisons to ambient water quality criteria (at the low end) and to elevated concentrations expected to be present if a strong PAH source is nearby (at the high end). The field and laboratory methods selected provide data of sufficient sensitivity to allow the project team to evaluate site conditions and meet the project objectives. Specific sensitivity requirements by target analyte in water are presented in Table 4. See Appendix B for an explanation as to how these analytical sensitivity requirements

were established. The laboratory will report results for PAHs down to the Method Detection Limit.

The resulting SPME contaminant concentration will be converted to freely dissolved porewater concentrations using the regression equations established as part of the SPME Calibration Study Report (Appendix A).

3.1.1 METHOD DETECTION LIMIT (MDL)

The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the compound or element concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the compound or element (Appendix B of 40 CFR 136).

3.1.2 METHOD QUANTITATION LIMIT (MQL)

The MQL represents the value for which the laboratory has demonstrated the ability to reliably quantitate target compounds and elements within prescribed performance criteria for the method performed. Operationally, the MQL is equivalent to the concentration of the lowest calibration standard in the initial calibration curve.

3.1.3 METHOD REPORTING LIMIT (MRL)

The MRL is a threshold value below which the laboratory reports a result of non-detected. It may be based on project-specific concentrations of concern, regulatory action levels, or sensitivity capability of method and instrument. The MRLs are adjusted based on the sample matrix and any necessary sample dilutions. Operationally, it is equivalent to the MQL adjusted based on the sample matrix and any necessary dilutions. Because of the general lack of matrix interferences by the SPME method, the MRL is expected to equal the MQL.

Table 4. Analytical performance standards for SPME samples

Parameter – Method	Surface Water Quality Standards, µg/L	Low-Level Limits, µg/L		QC Acceptance Criteria	
		MDL	MRL	LCS CL %	LCS/LCSD RPD
PAHs (SW-8310)					
Low Molecular Weight PAHs					
2-Methylnaphthalene	n/a	0.212	1.54	45-105	<25
Acenaphthene	$6.40x10^{2}$	0.335	0.732	35-105	<25
Anthracene	$2.64x10^{4}$	0.0515	0.322	40-110	<25
Fluorene	$3.46\ x10^{3}$	0.454	0.778	35-105	<25
Naphthalene	9.58	0.291	2.80	35-105	<25
High Molecular Weight PAHs					
Benzo(a)anthracene[c]	$1.80x10^{-2}$	$2.20x10^{-4}$	$5.70\ x10^{-4}$	50-110	<25
Benzo(a)pyrene[c]	$1.80x10^{-2}$	$1.10\ x10^{-4}$	$4.10\ x10^{-4}$	45-115	<25
Benzo(g,h,i)perylene[a, c]	n/a	$9.00\ x10^{-5}$	$2.70\ x10^{-4}$	35-120	<25
Benzo(b)fluoranthene[c]	$1.80x10^{-2}$	$3.90\ x10^{-4}$	$7.40\ x10^{-4}$	40-125	<25
Benzo(k)fluoranthene[c]	$1.80x10^{-2}$	$4.00\ x10^{-5}$	$4.60\ x10^{-4}$	45-125	<25
Chrysene	$1.80x10^{-2}$	$6.40\ x10^{-4}$	$1.29\ x10^{-3}$	50-115	<25
Dibenz(a,h)anthracene	$1.80x10^{-2}$	$3.00\ x10^{-5}$	$1.50\ x10^{-4}$	20-110	<25
Fluoranthene	90	$9.27\ x10^{-3}$	$6.13\ x10^{-2}$	50-115	<25
Indeno(1,2,3-cd)pyrene[a]	$1.80x10^{-2}$	$9.00\ x10^{-5}$	$2.70\ x10^{-4}$	45-110	<25
Phenanthrene	n/a	$4.93\ x10^{-2}$	$1.50x10^{-1}$	40-120	<25
Pyrene	$2.59x10^{3}$	$1.01x10^{-2}$	$3.38x10^{-2}$	50-110	<25
PAH Secondary Calibration Standard					
(Run At Initial Calibration; Relative to Primary Standard)					<15 [b]
Other Semivolatile Organic Compounds					
Dibenzofuran		$5.67x10^{-2}$	$5.79x10^{-1}$	65-135	<25

LCS – Lab calibration standard

LCSD – LCS duplicate

CL – Control limit

RPD – Relative Percent Difference

[a] – Benzo(g,h,i) perylene and Indeno(1,2,3-cd) pyrene co-elute and may not be analytically separated by the Laboratory, although efforts are underway to separate them.

[b] – This value is from the DOD QSM Table F2, for HPLC and water matrix.

c– The listed MRL is above the Surface Water Quality Standard concentration for these PAHs.

3.2 Quality Control

The overall quality assurance objective for field sampling and laboratory analysis is to produce data of known and appropriate quality to support the project objectives. Appropriate procedures and quality control checks will be used so that known and acceptable levels of accuracy and precision are maintained for each data set. Quality control samples are controlled samples introduced into the analysis stream whose results are used to review data quality and to calculate the accuracy and precision of the chemical analysis program. The purpose of each type of quality control sample, collection and analysis frequency, and evaluation criteria are described in this section. Laboratory quality control samples as described in the referenced methods will be followed.

All quality control measurements and data assessment for this project will be conducted on samples from and within batches of samples from this project alone; in other words, no "other project" samples will be used with samples from this project for assessment of data quality.

3.2.1 FIELD QUALITY CONTROL SAMPLES

Field quality control checks are accomplished through the analysis of controlled samples that are introduced to the laboratory from the field and include trip blanks, field duplicates and matrix spike/matrix spike duplicate (MS/MSD) samples. In this study, **trip blanks** and **field duplicates** (based upon adjacent segments of the SPME fiber) will be analyzed. As described in Section 2.3.5, **field duplicates** will be collected for all samples from adjacent fiber depth intervals. However, experience has suggested that results for the field duplicate samples will correlate highly with results for primary samples. Their primary purpose is to identify sample problems (such as cap unsealed) that might lead to evaporation of the contents or other problems that will compromise individual samples. **Solvent blanks** will be analyzed at the time of filling of the vials for shipment, i.e. one at the start of filling and one at the end where the same solvent source has been used. If these contain PAHs at significant levels, new vials will be filled with a separate source and the process will be repeated. **Sampler and fiber contamination check samples** will also be tested at the start and end of the cleaning procedures and analyzed prior to shipment. In addition, there will be solvent blanks shipped with the samples at a frequency of 1 per 20 samples. **Field blanks** will be the samplers shipped with the other samples but not placed at the site. One field blank will be included per shipping container. A total of 5, 2 cm sections will be collected from each field blank sample. The 2 cm sections will be collected at even distances spaced along the fiber. Due to the nature of the SPME sampling, no matrix spikes will be employed.

3.2.2 LABORATORY QUALITY CONTROL SAMPLES

Laboratory QC checks are accomplished through analyzing initial and continuing calibration samples, method blanks, surrogate spikes, laboratory control samples (LCS), and laboratory duplicate samples.

Initial and Continuing Calibration Samples. Calibration of laboratory owned and operated equipment will be in accordance with the laboratory quality assurance/quality control plan as described herein and laboratory standard operating procedures (SOPs); see Appendix A for the

following SOPs: total and dissolved organic carbon analysis, PAHs analysis by High Performance Liquid Chromatography, and liquid-liquid extraction for aqueous organics via separatory funnel.

Method Blanks. Method blanks are used to check for laboratory contamination and instrument bias. Laboratory method blanks will be analyzed at a minimum frequency of 5 percent or one per analytical batch for all chemical parameter groups. Quality control criteria require that no contaminants be detected in the blank(s) at concentrations greater than one-half the method quantitation limit (MQL) for target compounds and greater than the MQL for the common laboratory contaminants. If a chemical is detected, the action taken will follow the laboratory SOPs (provided in Appendix A). Blank samples will be analyzed for the same parameters as the associated field samples.

Surrogate Spikes. Surrogates are substances with properties that mimic the analyte of interest. A surrogate is unlikely to be found in environment samples, and is therefore added to them for quality control purposes. A sample will be spiked with a known quantity of the surrogate, and the amount of the surrogate recovered after analysis will be reported. This will help determine lab quality control factors with respect to analyzing this general type of chemical.

Laboratory Control Samples. Not applicable. Calibration check standards will be used to compare to and these will be in the same solvent at similar concentrations as the analyzed samples and will be handled in field the same way that primary samples are handled. A previous study (SPME Calibration Study, 2010 PSR Field Deployment Plan) showed that extraction is almost complete (>99%) in a couple of minutes, so no LCS samples are needed. Calibration check standards are sufficient for evaluating potential loss and contamination during sampling.

Laboratory Duplicate Samples. Precision of the analytical system is evaluated by using laboratory duplicate samples. Laboratory duplicate samples are two portions of a single homogeneous sample analyzed for the same parameter. Laboratory duplicate samples will be prepared and analyzed with project samples as listed in laboratory SOPs.

Table 5. Quality Guidelines for Organic Analysis by High-Performance Liquid Chromatography (EPA 8310) from DOD QSM Version 5.1.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	ICAL must meet one of the three options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression for each analyte: $r^2 \geq 0.99$; Option 3: non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT from the 72-hour study or 0.03 minutes, whichever is greater.	NA.	NA.	Calculated for each analyte and surrogate. Only applicable if internal standard calibration is not used.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within established RT windows. All reported analytes within ± 15% of true value.	Correct problem, rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Before sample analysis, after every 10 field samples, and at the end of the analysis sequence.	All reported analytes and surrogates within established RT windows. All reported analytes and surrogates within ± 15% true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Internal Standards (IS)	If employed, every field sample, standard and QC sample.	Retention time within ± 30 seconds from retention time of the midpoint standard in the ICAL; Internal standard signal (area or height) within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect HPLC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the Case Narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	NA.
Method Blank (MB)	One per preparatory batch.	No analytes detected > 1/2 LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid Method Blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for the failed reported analytes if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Surrogate Spike	All field and QC samples.	QC acceptance criteria specified by the project if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed.	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative.	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the Case Narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table B-2. Organic Analysis by High-Performance Liquid Chromatography (HPLC)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Confirmation of positive results (second column)	All results > the DL must be confirmed.	Calibration and QC criteria for second column are the same as for initial or primary column analysis. Results between primary and secondary column/detector RPD ≤ 40%.	NA.	Apply J-flag if RPD > 40%. Discuss in the Case Narrative.	Spectral match confirmation of a UV detector with a UV diode array detector (or vice versa) is not considered an acceptable confirmation technique. A second column confirmation is required. Use project-specific reporting requirements if available; otherwise, use method requirements if available; otherwise, report the result from the primary column.

3.2.3 ANALYTICAL DATA QUALITY INDICATORS

The data quality indicators presented in this section are precision, accuracy (bias), representativeness, comparability, completeness, and sensitivity. Project-specific control limits for these indicators are presented in Table 2 Appendix C.

Precision. Precision is defined as the degree of agreement between or among independent, similar, or repeated measures. Precision is expressed in terms of analytical variability. For this project, analytical variability will be measured as the relative percent difference (RPD) or coefficient of variation between results between the primary and secondary determinations of water and SPME extractions. The precision goal for this project is 35%.

Precision will be calculated as the RPD as follows:

$$\%RPD_i = \frac{2|O_i - D_i|}{(O_i + D_i)} \times 100\%$$

where:

$\%RPD_i$	=	Relative percent difference for compound *i*
O_i	=	Value of compound *i* in original sample
D_i	=	Value of compound *i* in duplicate sample

The resultant RPD will be compared to acceptance criteria and deviations from specified limits reported. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. The RPD will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewer.

Accuracy. Accuracy is the amount of agreement between a measured value and the true value. It will be measured as the percent recovery of standard samples versus the published value, verified by the secondary source verification standard.

Accuracy shall be calculated as percent recovery of target analytes as follows:

$$\%R_i = (Y_i \div X_i) \times 100\%$$

where:

$\%R_i$	=	percent recovery for compound *i*
Y_i	=	measured analyte concentration in sample *i* (measured - original sample concentration)
X_i	=	known analyte concentration in sample *i*

The resultant percent recoveries will be compared to acceptance criteria and deviations from specified limits will be reported. The second source verification standard limit is 25%. The

accuracy limit is 35%. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. Percent recoveries will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewer.

Representativeness. Representativeness is the degree to which sample results represent the system under study. In the present case, representativeness is addressed by the experimental design.

Comparability. Comparability is the degree to which data from one study can be compared with data from other similar studies, reference materials, and screening values. Comparability will be achieved through using standard techniques to collect and analyze representative samples and reporting analytical results in appropriate units.

Completeness. Completeness for usable data is defined as the percentage of usable data out of the total amount of planned data. The target goal for completeness is 95 percent for all data. Completeness for quality data shall be 95 percent for each individual analytical method. Quality data are data obtained in a sample batch for which all QC criteria were met. Completeness will be calculated as follows:

$$\%C = A / I \text{ x}100\%$$

where:

$\%C$	=	Percent completeness (analytical)
A	=	Actual number of samples collected/valid analyses obtained
I	=	Intended number of samples/analyses requested

Non-valid data (i.e., data qualified as "R" rejected) will be identified during the QA review.

Sensitivity. The sensitivity of the analytical methods (i.e., method reporting limits) identified for this project are sufficient to allow comparison of project results to decision criteria. Analytical method reporting limits for all requested analytes are listed in Table 4.

3.3 Laboratory Equipment Maintenance

Laboratory instrumentation will be examined and tested prior to being put into service and will be maintained according to the manufacturer's instructions. Sampling personnel will maintain a supply of typical maintenance replacement items available in the field to help prevent downtime because of equipment malfunctions. Examples of typical equipment maintenance items may include but not be limited sample containers and calibration standards.

All laboratory instruments will be maintained as specified in the project laboratory's QA plan and according to manufacturers' instructions. Manufacturer's instructions will be followed for any additional equipment that is required for the project.

3.4 Instrument Calibration

Laboratory instrument calibration will be conducted in accordance with the QC requirements identified in the manufacturers' instructions and the laboratory SOPs. General requirements are discussed below.

3.4.1 LABORATORY INSTRUMENTS

Calibration of all analytical instrumentation is required to ensure that the analytical system is operating correctly and functioning at the sensitivity required to meet project objectives. Each instrument will be calibrated with standard solutions appropriate to the instrument and analytical method, in accordance with the methodology specified and at the QC frequency specified in the laboratory SOPs (Provided in Appendix A).

The calibration and maintenance history of the fixed laboratory instrumentation is an important aspect of the project's overall QA/QC program. As such, all initial and continuing calibration procedures will be implemented by trained personnel following the manufacturer's instructions and in accordance with applicable EPA protocols to ensure the equipment is functioning within the tolerances established by the manufacturer and the method-specific analytical requirements.

3.4.2 STANDARD SOLUTIONS

A critical element in the generation of quality data is the purity/quality and traceability of the standard solutions and reagents used in the analytical operations. To ensure the highest purity possible, all primary reference standards and standard solutions will be obtained from a reliable commercial source. The laboratories will maintain a written record of the supplier, lot number, purity/concentration, receipt/preparation date, preparer's name, method of preparation, expiration date, and all other pertinent information for all standards, standard solutions, and individual standard preparation logs.

Standard solutions will be validated prior to use. Validation procedures can range from a check for chromatographic purity to verification of the concentration of the standard solution using another standard solution prepared at a different time or obtained from a different source. Stock and working standard solutions will be checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change of concentration. Care will be exercised in the proper storage and handling of standard solutions, and all containers will be labeled as to compound, concentration, solvent, expiration date, and preparation data (initials of preparer/date of preparation). Reagents will be examined for purity by subjecting an aliquot or subsample to the corresponding analytical method as well.

3.5 Data Management

All project data and information must be documented in a format that is usable by project personnel in a manner that ensures data integrity, defensibility, and retrieval. The procedures describing how project data and information will be documented, tracked, and managed, from generation in the field to final use and storage are described in general below. Data will be generated by Texas Tech using manual notebooks and computers. The documentation report shall describe the Texas Tech:

- Team roles and responsibilities
- Data sources
    - Existing
    - New
- Software
    - Data conversion software used to import existing data
    - Data entry, review, and editing software
    - Analysis, modeling, and presentation software
- Hardware
- Documentation requirements
- Security procedures

Data will be provided to the Seattle District Corps of Engineers as a report and worksheet or database files. The Seattle District has a Data Management Program in place.

3.5.1 PROJECT DOCUMENTATION AND RECORDS

Project documents and records that will be generated for this project are described in the following sections.

Analytical Records

- Chain-of-custody records
- Sample receipt forms and sample tracking forms
- Preparation and analysis forms and/or logbooks
- Tabulated data summary forms and raw data for field samples, standards, QC checks, and QC samples
- Case narrative
- Sample chronology (time of receipt, extraction, and analysis)
- Identification of QC samples
- Communication logs
- Corrective action reports
- Definitions of laboratory qualifiers
- Documentation of corrective action results

- Documentation of laboratory method deviations
- Electronic data deliverables
- Instrument calibration reports
- Laboratory name
- Laboratory sample identification numbers
- Reporting forms, completed with actual results
- Signatures for laboratory sign-off (e.g., laboratory QA manager)
- Standards traceability records
- Other relevant project-specific documents in the laboratory's possession, such as telephone logs, MDL studies, initial precision and accuracy tests, and corrective action reports

Project Data Assessment Records

The following records will be retained by the Seattle District Project Manager or Technical Team Leader:

- Analytical audit checklists (when applicable)
- PT sample results (when applicable)
- Data review reports
- Telephone logs
- Corrective action reports
- Laboratory assessment (when applicable)
- Laboratory QA plan
- MDL study information

3.5.2 DATA PACKAGE DELIVERABLES

Results for fixed-based analyses will include the elements listed below:

- Case narrative
    - Airbills
    - Chain-of Custody Records (Traffic Reports)
    - Sample Tags
    - Sample Log-In Sheet

- Miscellaneous Shipping/Receiving Record
- Internal Lab. Sample Transfer Records and Tracking Sheets

- Sample Data:
  - Chromatograms from all columns for each sample
  - Other analytical raw data
- Standards Data:
  - Method Detection Limit Study Tabulated Summary Form
  - Initial Calibration Tabulated Summary
  - Continuing Calibration Tabulated Summary
  - Standards preparation logbook pages
- QC Data:
  - Surrogate Percent Recovery Tabulated Summary
  - Method Blank Tabulated Summary Form
  - Internal Standard Area and RT Tabulated Summary Form
  - QC Raw Data - chromatograms, quantitation reports, integration reports etc.
  - QC sample preparation logbook pages
- Miscellaneous Data:
  - Original preparation and analysis forms or copies of preparation and analysis logbook pages
  - Screening records (when applicable)
  - All instrument output, including strip charts, from screening activities (when applicable)
  - Preparation logs raw data
  - Other records (e.g., telephone communication log)

3.5.3 DATA REPORTING FORMATS

To ensure that project data are sufficient to meet both qualitative and quantitative DQO, laboratory data deliverables permitting a data quality assessment are required. Laboratory deliverables will be sufficient to permit a limited quality review of precision, accuracy, and adherence to the method SOP.

Information provided will be sufficient to review the data with respect to the following:

- Holding times and conditions
- Detection/quantitation limits\
- Initial and continuing calibration
- Laboratory Control Samples
- Precision and accuracy
- Representativeness
- Comparability
- Completeness

Fixed Laboratory Deliverables. The laboratory will prepare and retain full analytical and associated QC documentation. The laboratory will report the data along with associated QC reporting data. The final analytical data will be provided in a limited deliverable data format as described in this section.

The analytical results will be submitted to the USACE via hard copy and electronic files. The laboratory is responsible for ensuring that all EDD are free of errors and match the hard copy reports.

Hard Copy Deliverables. The laboratory will provide the following hard copy information for each analytical data package submitted for this project:

- The cover sheet will list the samples included in the report, provide narrative comments describing problems encountered in analysis, and identify any analyses not meeting QC criteria, including holding times.
- Chain of custody forms and cooler receipt forms will be provided.
- Detailed tabulated results will be provided in electronic form with inorganic and organic compounds identified and quantified, and reporting limits for all compounds and elements shown. All compounds and elements will be reported for each sample as a detected concentration or as not detected above the specific limits of quantitation, which must be stated. The laboratory will also report dilution factors, date of extraction, extraction batch number, date of analysis, and analytical batch number for each sample.
- Analytical results will be provided for QC sample spikes, laboratory duplicates, initial and continuing calibration verifications of standards and laboratory blanks, standard procedural blanks, LCS or equivalent, surrogates, laboratory reference materials, and detection limit check samples.
- Raw data system printouts (or legible photocopies) will be provided that identify date of reported analysis, analyst, parameters analyzed, calibration curves, calibration verifications, method blanks, any reported sample dilutions, cleanup logs, laboratory

duplicates, spikes, control samples, sample spiking levels, preparation/extraction logs, run logs, and chromatograms.

- Chromatograms will be labeled with compound peaks, internal standards, and surrogate standards where applicable.
- The narrative accompanying the data package will include the identification of samples not meeting total QC criteria as specified in this QAPP, and/or the laboratory QA plans, and cautions regarding non-quantitative usability due to out-of-control QC results. Data reduction and QC review steps will be documented, signed, and dated by an authorized representative.

3.5.4 ELECTRONIC DATA MANAGEMENT

The USACE chemist is responsible for the organization and operation of the electronic data management. All electronic deliverables of data will be input into the USACE chemical database management system, EQuIS. EQuIS will track and report the following information:

- Sample collection information including sample number, station, matrix, type of sample (field, blank, duplicate), date of collection, and sampler.
- Analytical results including concentration, units, qualifier and analytical method. Results shall also be provided in a format suitable for presentation in a report, with qualifiers indicated and associated descriptions included as footnotes where needed.

Laboratory electronic data deliverables will be directly loaded into the database management system, thereby avoiding hand-entry errors. After data quality review is performed, the changes in values or qualifiers will be incorporated into the project database by Seattle District. The project manager will provide additional information such as sampling date, location coordinates, and depth interval from field sampling documentation forms, which are added to the database.

4.0 Assessment and Oversight

4.1 Assessments and Response Actions

The ultimate responsibility for maintaining quality throughout the monitoring program rests with the USACE Project Manager. The day-to-day responsibility for ensuring the quality of the laboratory data rests with the Technical Team Lead, QA manger, chemist, and the laboratory project manager or Principal Investigator.

Any non-conformances with the established QC procedures will be expeditiously identified and controlled. Where procedures are not in compliance with the established protocol, corrective actions will be taken immediately. Subsequent work that depends on the nonconforming activity will not be performed until the identified non-conformance is corrected.

No routine auditing is currently scheduled for this project. However, if problems are encountered that warrant further examination, performance and systems audits may be conducted to determine whether the following have occurred:

- The QA program has been documented in accordance with specified requirements.
- The documented program has been implemented.
- Any non-conformances were identified and corrective action or identified deficiencies were implemented.

4.1.1 PERFORMANCE AUDITS

Not applicable.

4.1.2 SYSTEMS AUDITS

No systems audits are proposed for this sampling and analysis sequence.

4.1.3 AUDIT PROCEDURES

No systems audits are proposed for this sampling and analysis sequence.

4.1.4 ASSESSMENT FINDINGS AND CORRECTIVE ACTION RESPONSES

The Technical Team Lead or designated representative will respond to the audit report within seven days of receipt. The response will clearly state the corrective action for each finding, including action to prevent recurrence and the date the corrective action will be completed.

Follow-up action will be performed by the Technical Team Lead, QA Manager, or a designated representative to accomplish the following:

- Evaluate the adequacy of the USACE response
- Evaluate that corrective action is identified and scheduled for each finding
- Confirm that corrective action is accomplished as scheduled

Follow-up action may be accomplished through written communications, re audit, or other appropriate means. When all corrective actions have been verified, a memo will be sent to the USACE Project Manager and the EPA RPM signifying the satisfactory closeout of the audit.

Field Corrective Action.

Not applicable.

Laboratory Corrective Action. The laboratory QA data reviewer will review the data generated to ensure that all QC samples have been run as specified in the protocol. The following will be evaluated against the control limits listed in Appendix A: recoveries of LCSs and surrogates; and RPD for laboratory duplicates for consistency with method precision; and QC samples for analyses.

Laboratory personnel will be alerted that corrective actions are necessary if any of the following occur:

- The QC data are outside the warning or acceptance windows established for precision and accuracy. The laboratory PM will contact the laboratory QA manager to discuss out-of-control-limit data sets. If the analyses cannot produce data sets that are within control limits, the Technical Team Lead will be notified within 48 hours of any analysis that fails to meet the DQOs specified in this QAPP.
- Blanks contain contaminants at concentrations above the levels specified in the laboratory QA plan for any target compound.
- Undesirable trends are detected in LCS recoveries, RPDs or surrogate recoveries.
- Unusual changes in detection limits are observed.
- Deficiencies are detected by the laboratory QA manager during internal or external audits, or from the results of PE samples.

If any non-conformances in analytical methodologies or QC sample results are identified by the analyst, corrective actions will be implemented immediately. Specific corrective actions are outlined in each laboratory method SOP (see Appendix C) and the Quality Assurance Surveillance Plan (Appendix D). Corrective action procedures will be handled initially at the bench level by the analyst, who will review the preparation or extraction procedure for possible errors, check the instrument calibration, spike and calibration mixes, instrument sensitivity, etc.

The analyst will immediately notify his/her supervisor of the identified problem and the investigation that is being conducted. If the problem persists or cannot be resolved, the matter will be referred to the laboratory supervisor and laboratory QA manager for further investigation. Once resolved, full documentation of the corrective action procedure will be filed by the laboratory QA manager in accordance with Appendix D.

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Corrective actions may include, but will not be limited to the following:

- Reanalyzing suspect samples if holding time criteria permit.
- Re-exposing and analyzing new samples.
- Evaluating and amending sampling and/or analytical procedures (with USACE consultation).
- Accepting data with an acknowledged level of uncertainty (with USACE consultation).
- Recalibrating analytical instruments.
- Evaluating and attempting to identify limitations of the data

Data deemed unacceptable following the implementation of the required corrective action measures will not be accepted by the Technical Team Lead and follow-up corrective actions will be explored.

Corrective Actions Following Data Evaluation. The Technical Team Lead, or a designated party, will review the laboratory data generated for this project to ensure that all project QA objectives are met. If any non-conformances are found in the laboratory analytical and documentation procedures, and data evaluation and quality review procedures, the impact of those non-conformances on the overall project QA objectives will be assessed. Appropriate actions, including re-sampling and reanalysis, may be recommended in accordance with Appendix D, so that the project objectives can be accomplished. Any corrective actions required will be documented in a formal memorandum and submitted to the USACE PM.

4.1.4 AUDIT RECORDS

Original records generated for all audits will be retained in the central project files. Records will include audit reports, written replies, the record of completion of corrective actions, and documents associated with the conduct of audits that support audit findings and corrective actions as appropriate.

4.2 Final Project Reports

Field activities will be documented in a draft and final reports. The report will include the following:

- Summary of activities and identification of any deviations from this QAPP
- Tabulation of all laboratory data
- Descriptions of data analysis performed
- Interpretations of results in relation to the purpose and objectives of the project activities. This narrative will include a summary of study results and utility of SPME use quantitative measurements of compliance with surface water quality standards where such standards exist.
- Identification of areas where additional investigation may be needed

- Data quality review reports
- Data quality assessment summary

Forms, notes, and original laboratory data will be stored in the project files and will not be reproduced for these reports.

Draft reports will be submitted to EPA for review and comment. If necessary, a review conference may be held to discuss and clarify comments prior to production of the final reports.

5.0 Data Validation and Usability

5.1 Data Review, Verification, and Validation

The purpose of the data quality review is to eliminate unacceptable analytical data and to designate a data qualifier for any data quality limitation discovered. Stage 2b analytical data validation will be performed. This includes a review of laboratory performance criteria and sample-specific criteria. The reviewer will determine whether the measurement quality objectives have been met, and will calculate the data completeness for the project.

Data quality reviews will be conducted by Texas Tech, and confirmed by USACE Seattle District.

Data quality review consists of a review of the data summary forms that are generated for a set of data. At a minimum, chain-of-custody records, the case narrative, and the summary results for project samples and quality control samples are reviewed. The data are reviewed in accordance with the criteria contained in EPA guidance documents modified for the analytical method used.

The data quality review will include verification of the following:

- Compliance with this QAPP
- Proper sample collection and handling procedures
- Holding times
- QC results
- Instrument calibration verification
- Laboratory blank analysis
- Detection and MRL
- Laboratory duplicate precision
- Data completeness and format
- Data qualifiers assigned by the laboratory
- Surrogate compound recoveries
- Primary and secondary column verification
- Instrumentation calibration linearity

Qualifiers will be added to data during the review as necessary. Common, but not all, qualifiers applied to the data as a result of the review are:

U The analyte was analyzed for but was not detected above the reporting limit.

J The analyte was detected at a concentration less than the laboratory reporting limit, and the result is therefore considered an estimated quantity.

UJ The analyte was not detected above the sample reporting limit. However, the reporting limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified. No associated value is reported.

Results of the data quality review will be included in a data quality review report that will provide a basis for meaningful interpretation of the data quality and evaluate the need for corrective actions and/or comprehensive data validation.

5.1.1 DATA REVIEW PROCESS

The chemical data review process for this project will include data generation, data reduction, and two levels of QA review. The first level of QA review will be conducted by the laboratory prior to submittal of the electronic and hardcopy data to the USACE. After receipt of data packages, a data quality review will be performed in accordance with this QAPP.

Field Measurement Quality Assurance. The Technical Lead (Bill Gardiner) is responsible for field quality assurance. She will review the deployment, retrieval and sample preparation documentation for consistency with established protocols. Field notes will be reviewed and checked for completeness and legibility. Where procedures are not strictly in compliance with established protocol, the deviations will be field documented and reported to the QA Manager. All corrective actions will be defined, documented, and implemented by the Technical Lead. A Quality Assurance Report will be filed for the field activity.

Laboratory Data Quality Assurance/Quality Control. Laboratory quality assurance will be reviewed by the laboratory according to the requirements in this QAPP, based upon the DOD QSM Version 5.1. The USACE chemist will verify all qualified data. The USACE chemist may edit a qualifier based on his or her professional judgment, which may include reviewing hardcopy data packages to resolve issues.

5.1.2 DATA INTERPRETATION

Site investigation results will be presented in text, tables, and graphics. Text will be in Microsoft Word format. Tabular data will be presented in Microsoft Excel format. Data will be exported from the project database to Excel for preparation of reports and other documents.

5.2 Reconciliation with User Requirements

Following the analyses, reporting, and data quality reviews have been completed, a data quality review report will be prepared. In this report, all data generated for this project will be reconciled with the project objectives.

References

Department of Defense (DOD). Quality Systems Manual for Environmental Laboratories, Version 4.1. 2006. http://www.navylabs.navy.mil/QSM%20Version%204.1.pdf

Mayer P, Vaes WHJ, Hermens JLM. 2000. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: high partition coefficients and fluorescence microscopy images. Anal Chem 72: 459-464.

Pawliszyn, J. Solid phase microextraction, theory and application, 1996, Wiley-vch,Inc., NY,USA.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 3510C. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

Reible, D. G Lotufo, A Skwarksi, L Lampert, XiaoXia Lu. 2008. Laboratory Study Report, Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility. ESTCP Project ER-0624. http://www.estcp.org/Technology/upload/ER-0624-Lab-Rep.pdf

Reible, D. (2010) Final Report on Calibration Study, April 26, 2010, University of Texas, Austin, TX 78712

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FIGURES

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Figure 1. Push-point sampler in the lab (upper) and insertion into intertidal sediment in the field (lower).

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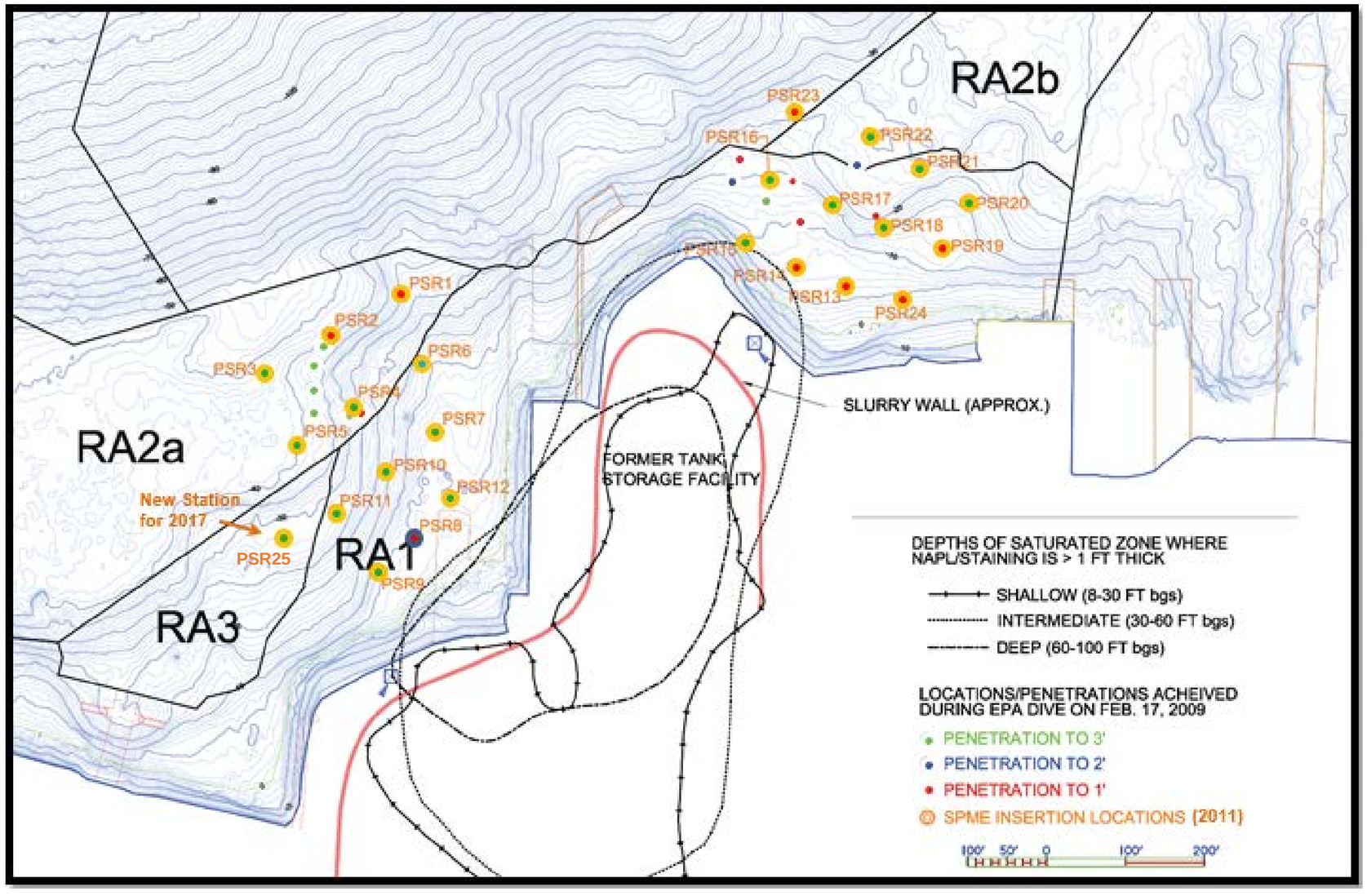

Figure 2. SPME sampling locations PSR1 – PSR25 shown in orange.

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Figure 3

Figure 3. SPME background surface water sample will be deployed (by a diver) ~ 100 ft off of condo pilings.

Figure 4. Placement of the SPME fiber inside the push-point sampler.

TABLES

Table 6. Sample transect deployment locations (northing/easting)

Sample ID	Location	End Transect Coordinate	Northing/Easting
Transect 1			
PSR-9	47 35 02.12337, -122 22 10.74519		Start: 47.58392 N -122.36970 W
PSR-11	NW of PSR-9, 90 ft		
PSR-5	NW of PSR-11, 100 ft		
PSR-3	NW of PSR-5, 100 ft	47 35 04.56950, -122 22 12.87703	End: 47.584889 N -122.370244 W
Transect 2			
PSR-8	47 35 02.56486, -122 22 10.06272		Start: 47.58416 N -122.36957 W
PSR-10	NW of PSR-8, 95 ft		
PSR-4	NW of PSR-10, 95 ft		
PSR-2	NW of PSR-4, 95 ft	47 35 05.06818, -122 22 11.71077	End: 47.58513 N -122.37003 W
Transect 3			
PSR-12	47 35 03.06821, -122 22 09.41184		Start: 47.58457 N -122.36936 W
PSR-7	NW of PSR-12, 90 ft		
PSR-6	NW of PSR-7, 90 ft		
PSR-1	NW of PSR-6, 95 ft	47 35 05.59990, -122 22 10.41015	End: 47.58561 N -122.36960 W
Transect 4			
PSR-15	47 35 06.32808, -122 22 04.06826		Start: 47.58032 N -122.36947 W
PSR-16	NE of PSR-15, 90 ft		
PSR-23	NE of PSR-16, 90 ft	47 35 07.97306, -122 22 03.19982	End: 47.585548 N -122.367555 W
Transect 5			
PSR-14	47 35 06.03247, -122 22 03.13466		Start: 47.58511 N -122.36756 W
PSR-17	NE of PSR-14, 90 ft		
PSR-22	NE of PSR-17, 95 ft	47 35 07.68645, -122 22 01.80334	End: 47.58558 N -122.36699 W
Transect 6			
PSR-13	47 35 05.81359, -122 22 02.18920		Start: 47.58504 N -122.36720
PSR-18	NE of PSR-13, 90 ft		
PSR-21	NE of PSR-18, 90 ft	47 35 07.31283, -122 22 00.85498	End: 47.58578N -122.36668 W
Transect 7			
PSR-24	47 35 05.65930, -122 22 01.13815		Start: 47.585 N -122.36695
PSR-19	NE of PSR-24, 90 ft		
PSR-20	NE of PSR-19, 90 ft	47 35 06.87505, -122 21 59.96630	End: 47.58542 N -122.36655 W
Additional, new sample location			
PSR-25	SW of PSR-11, 70 ft		
	PSR-11 Coord:	47 35 02.85564, -122 22 11.52166	47.584127 N -122.369867 W
	PSR-25 Coord:	47 35 02.69, -122 22 12.34	47.584081 N -122.370094 W

Table 7. GPS Locations of Sample Points (latitude/longitude)

Sample Location	Latitude	Longitude
PSR-1	47 35 05.59990	122 22 10.41015
PSR-2	47 35 05.06818	122 22 11.71077
PSR-3	47 35 04.56950	122 22 12.87703
PSR-4	47 35 04.16900	122 22 11.23539
PSR-5	47 35 03.68466	122 22 12.25316
PSR-6	47 35 04.74263	122 22 09.99683
PSR-7	47 35 03.88236	122 22 09.70902
PSR-8	47 35 02.56486	122 22 10.06272
PSR-9	47 35 02.12337	122 22 10.74519
PSR-10	47 35 03.37492	122 22 10.63033
PSR-11	47 35 02.85564	122 22 11.52166
PSR-12	47 35 03.06821	122 22 09.41184
PSR-13	47 35 05.81359	122 22 02.18920
PSR-14	47 35 06.03247	122 22 03.13466
PSR-15	47 35 06.32808	122 22 04.06826
PSR-16	47 35 07.12536	122 22 03.63594
PSR-17	47 35 06.81828	122 22 02.48346
PSR-18	47 35 06.55796	122 22 01.53811
PSR-19	47 35 06.30655	122 22 00.42228
PSR-20	47 35 06.87505	122 21 59.96630
PSR-21	47 35 07.31283	122 22 00.85498
PSR-22	47 35 07.68645	122 22 01.80334
PSR-23	47 35 07.97306	122 22 03.19982
PSR-24	47 35 05.65930	122 22 01.13815
PSR-25	47 35 02.69	122 22 12.34

APPENDIX A

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STANDARD OPERATING PROCEDURE: Total and Dissolved Organic Carbon Analysis

1.0 Purpose/Applicability

This SOP is based upon Standard Method 5310b and is applicable in determining the amount of dissolved organic carbon in PSR-derived seawater.

2.0 Summary of Method

A measured volume of sample, here is 40 mL, is analyzed for dissolved organic carbon using Tekmar Dohrmann Apollo 9000.

3.0 Interferences

Unwanted organic chemicals can be introduced into the sample extract through contaminated reagents, glassware, chemicals or through poor technique. Sample blanks are analyzed to insure that contaminants are not introduced into the sample extract.

4.0 Apparatus

The Tekmar Dohrmann Apollo 9000 consists of an IC sparger, furnace, moisture control system, corrosives scrubber and the non dispersive infrared detection system (NDIR).

5.0 Operating Conditions

The Tekmar Dohrmann Apollo 9000 operates at 670ºC. The injection volume of the sample is 0.5mL and the sparge volume is 0.5 mL. The TOC method used in the quantification of DOC, first acidifies the sample in the IC sparger unit (removing inorganic carbon) and then combusts the sample to carbon dioxide. The carbon dioxide is then swept away with a carrier gas into the NDIR system.

6.0 Reagents

Carbon Stock Standard (SS) (1000mg/L)
Primary dilution standard (PDS) (100mg/L)
Phosphoric Acid (reagent grade and 20%)

7.0 Standards Preparation and Standard Curve

7.1 SS- 1000 mg/L carbon stock standard is prepared by dissolving 212.54mg of dried (at 103ºC for 2 hours) and cooled potassium hydrogen pythalate into a total volume of 100 mL DI water. 100uL of reagent grade phosphoric acid is added to prevent bacterial degradation of the standard. This standard can be stored for up to 1 month in 4ºC.

7.2 PDS- 10mL of the above 1000mg/L SS is diluted with DI to 100mL. This 100 mg/L PDS will be diluted further to get the following concentrations: 1, 2, 4, 5, and 10mg/L standards. Two drops of reagent grade phosphoric acid is added to these standards which can be stored for up to one month.

7.3 DOC Standards of 1, 2, 4, 5, and 10mg/L are analyzed on the Tekmar Dohrmann Apollo 9000. A response factor (RSF) is determined, with units of concentration/response, by plotting the DOC concentration versus the Apollo 9000's NDIR measurements. The slope of the linear curve with an intercept of zero is this RSF.

8.0 Sample Procedure

8.1 After equilibrium is established for the PSR-derived seawater calibration sample (spiked with 16PAH, DBF and 2-MNP), 40mL is transferred to a new 40mL vial.

8.2 Two drops of reagent grade phosphoric acid is added to the sample. The sample is capped with a Teflon-lined screw cap and can be stored at 4ºC for no longer than three weeks prior to analysis.

8.3 Turn on the Apollo 9000 and open the Oxygen supply. Ensure 20% Phosphoric acid and DI water are available for the run.

8.4 Load samples to the sample rack.

8.5 Set up the sample run with selecting the appropriate method.

8.6 Initiate run and verify the needle is automatically rinsed with DI water to prevent cross sample contamination.

8.7 After the run is complete, shut down the system and record data.

9.0 Calculation

9.1 Using the standard curve established in part 7.0, the DOC content in the PSR-derived seawater calibration sample can be calculated. The NDIR measurements for the samples multipled by RSF gives the DOC concentration in the samples.

10.0 Quality Control

10.1 All quality control data should be maintained and available for easy reference or inspection.

10.2 At least two Milli-Q water sample blanks will be analyzed for the five point calibration curve to determine background DOC concentration.

10.3 PSR-derived seawater sample blanks (not spiked) will be analyzed to compare the background DOC concentration.

Reference APHA, AWWA and WEF. 1992. Method 5310 Total Organic Carbon (TOC). *Standard Methods for the Examination of Water and Wastewater 18Ed*.

STANDARD OPERATING PROCEDURE: PAH analysis by High Performance Liquid Chromatography (HPLC)

1.0 Purpose/Applicability

This SOP is based on EPA standard method 8310 in SW846 series. This method is developed for polycyclic aromatic hydrocarbons (PAHs), but is applicable to Dibenzofuran (DBF). This method works for all matrices, water, fiber and sediment.

2.0 Interferences

Unwanted organic chemicals can be introduced into the samples through contaminated reagents, glassware, chemicals or through poor technique. Reagent and sample blanks are analyzed to insure that contaminants are not introduced into the samples.

3.0 Apparatus

The HPLC model is Waters 2795 (Waters, Milford, MA, USA) with ultraviolet-diode array (PAD 996) and fluorescence detectors (FLD 2475). The column is Phenomenex (Torrance, CA, USA) Luna 5µ C18 column (250*4.6 mm).

4.0 Operating conditions

4.1 HPLC is operated at isocratic condition. The mobile phase is acetonitrile (ACN) and water. The flow rate is 1.0 ml/min, and the ACN to water ratio is 70 % ACN and 30% water. The temperature is set at 40 ºC

4.2 Emission and excitation wavelengths used for different PAHs in fluorescence detector are optimized to give good sensitivity as shown in the following table

Table 1 Emission and excitation wavelengths for selected PAHs

	Naph-thalene	Dibenzofuran 2-Methylnaphthalene Fluorene Acenaphthalene phenanthrene	Anthra-cene	Fluoranthene pyrene	Chrysene B[a]A	B[b]F B[k]F B[a]P Dibenz[ah]A Benzo[ghi]p Indino[123-cd]P
Excitation(nm)	280	270	305	305	295	305
Emission (nm)	340	360	405	430	385	430

5.0 Reagents

5.1 Mobile phases: HPLC grade acetonitrile and water, or high purity water from Milli-Q water treatment equipment.

5.2 Standard stock solutions: The standard stock solution for calibration may be purchased or prepared from ultrahigh purity grade chemicals. The standard stock solution for 16PAHs was purchased from Ultra Scientific, and 2-MNP and DBF were made from ultrahigh purity solid. This stock solution is made with high concentrations and a secondary stock solution was prepared by diluting a certain volume of the stock solution in volumetric flask. The secondary stock solution is used to make calibration standards.

5.3 Second source check standard: stock standard from another source like Supelco is purchased to check the reliability or accuracy of the calibration curves.

5.3 Mixed calibration standards: Calibration standards are prepared by combining appropriate volumes of secondary stock solutions in volumetric flasks.

6.0 Procedure

6.1 Set up the instrument with a proper method (all the operating parameters are included in operating conditions). The instrument must be allowed to become stable (stable flow, temperature, and pressure) before each analysis.

6.2 Turn on the detectors and retrieve appropriate method for fluorescence detector (emission and excitation wavelengths as defined in operating conditions)

6.3 load samples to autosampling tray

6.4 set up sample set table

6.5 press “run” button to start samples

6.6 Check if the autosampler selects the appropriate vial, and check if signals from UV and FLD are normal.

6.7 shut down flow and detectors after finishing all samples

7.0 Calculation

7.1 Minimum five-point calibration is conducted prior to analysis. Usually seven or eight concentrations are prepared. Remove concentrations that can not be detectable and concentrations that are beyond the linear range of the detector.

7.2 Determine the response factor (RSF) for each compounds: plotting chromatographic peak areas versus the concentrations, the slope of the linear curve after forcing to zero is the RSF(area/concentration) of each compound. This is applicable only if the calibration curve is linear in the range of interest and if the intercept from a calibration not forced to zero is below the quantitation limits for the analysis of interest. In general, the reciprocal of this RSF is more convenient to use and is frequently called RSF (concentration/area) in this analysis.

7.3 Determine the concentration in final solvent: the chromatographic peak areas of your samples times the RSF give the concentrations in your samples.

7.0 Quality control

Quality control checks of this SOP are based upon the DOD quality guidelines for organic analysis by high-performance liquid chromatography and slightly modified to meet specific project goals. The details of the quality control checks are summarized in Table 2.

LCS standards are also based upon DoD guidelines and are contained in the Appendix for both liquid and solid samples.

TABLE 2. SUMMARY OF QUALITY CONTROL CHECKS, DEFINITION, PURPOSE, MINIMUM FREQUENCY AND ACCEPT CRITERIA

	Definition	Purpose	Minimum frequency	Acceptance criteria
Demonstrate acceptable analyst capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analyst's ability to produce data of acceptable accuracy and precision.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria
Initial calibration for all analytes (ICAL)	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.	To establish a calibration curve for the quantification of the analytes of interest	Minimum five-point Initial calibration for all analytes Initial calibration prior to sample analysis	linear least squares regression: $r \geq 0.995$ (r^2>0.99)
calibration verification (CV)	The verification of the initial calibration that is required during the course of analysis at periodic intervals	To verify that Instrument response is reliable, and has not changed significantly from the current initial calibration curve.	Initial calibration verification (ICV) Before sample analysis. Continue calibration verification (CCV): after every 10 field samples and at the end of the analysis sequence Response factors of the initial and end check standard added to the control chart	All analytes within ± 20% of expected value from the ICAL
Second source calibration verification (ICV)	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration.	Minimum three-point check Once after initial calibration for at least 80% of analytes	All project analytes should be within the established retention windows and the response factors of all analytes are within 20% of the expected value from ICAL.
Method detection limit (MDL) study	The process to determine the minimum concentration of a substance (analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero	At initial set-up, new method is set up or new calibrations are initiated, otherwise once per 12 month period; otherwise quarterly MDL verification checks shall be performed	MDL verification checks must produce a signal at least 3 times the instrument's noise level.
Method blank	A sample of a matrix similar to the batch of associated samples (when available) in which no target analytes or interferences are present at concentrations that impact the analytical results. It is processed simultaneously with samples of similar matrix and under the same conditions as the samples.	To assess background interference or contamination in the analytical system that might lead to high bias or false positive data. Results of method blanks provide an estimate of the within-batch variability of the blank response and an indication of bias introduced by the preparation and analytical procedure	One per preparatory batch	No analytes detected > ½ RL (reporting limit). For common laboratory contaminants, no analytes detected at > RL, or does not interference with sample concentration
Reagents blank	The solvent used for preparing samples	To check the possible interference from the solvent, and clean the system for possible carryover	Before initial run, every 10 samples or one group of samples, and	No analytes detected > ½ RL (reporting limit). Or does not interference with sample concentration
Laboratory control sample (LCS) containing all analytes required to be reported (LCS samples are not applicable to this study; see Section 3.2.2)	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is analyzed using the same sample preparation, reagents, and analytical methods employed for regular samples.	To evaluate method performance by assessing the ability of the laboratory/analyst to successfully recover the target analytes from a control (clean) matrix. Control limits for LCS recovery, typically expressed as percent recovery, are used for the development of statistical control limits and serve as acceptance criteria for determining whether an analytical run is in control	Triplicates before new method and new matrix, then repeated as necessary (not applicable to water samples for direct injection and SPME fiber samples that do not involve sample transition)	DoD generated LCS-CLs will be used if available (see appendix)
Duplicate sample (replicate)	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are prepared and analyzed identically	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intra-laboratory analytical process for a specific sample matrix	A minimum three replicates for identification of mean, and at least four replicates for statistical analysis	RPD ≤ 20%

If any of the acceptance criteria are not satisfied, correct the problem and redo the quality control check.

APPENDIX

TABLE A1 LCS CONTROL LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS SW-846 METHOD 8310 WATER MATRIX

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	70	11	35	105	25	115
Acenaphthylene	74	13	35	115	20	125
Anthracene	77	12	40	110	30	125
Benz[a]anthracene	81	11	50	110	40	125
Benzo[a]pyrene	79	11	45	115	35	125
Benzo[b]fluoranthene	82	10	50	110	40	125
Benzo[k]fluoranthene	79	10	50	110	40	120
Benzo[g,h,i]perylene	77	14	35	120	20	135
Chrysene	83	11	50	115	40	125
Dibenz[a,h]anthracene	64	15	20	110	10	125
Fluoranthene	82	11	50	115	35	125
Fluorene	69	11	35	105	25	115
Indeno[1,2,3-cd]pyrene	80	11	45	110	35	125
Naphthalene	68	12	35	105	20	115
Phenanthrene	80	13	40	120	25	135
Pyrene	80	9	50	110	45	115

TABLE A2 LCS CONTROL LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS SW-846 METHOD 8310 SOLID MATRIX

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	71	12	35	110	20	120
Acenaphthylene	73	13	35	115	20	125
Anthracene	86	13	45	125	35	140
Benz[a]anthracene	78	9	50	105	40	115
Benzo[a]pyrene	86	15	40	135	25	150
Benzo[b]fluoranthene	89	11	55	120	45	130
Benzo[k]fluoranthene	84	12	50	120	35	135
Benzo[g,h,i]perylene[20]	85	10	55	115	45	125
Chrysene	87	11	55	120	45	130
Dibenz[a,h]anthracene	81	11	45	115	35	125
Fluoranthene	88	16	40	135	25	150
Fluorene	76	10	45	105	35	115
Indeno[1,2,3-cd]pyrene	95	13	55	135	45	145
Naphthalene	80	11	50	110	40	120
Phenanthrene	91	12	55	125	45	135
Pyrene	82	11	50	115	40	125

ReferenceU.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 8310. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

STANDARD OPERATING PROCEDURE: Liquid-liquid extraction for aqueous organics via separatory funnel

Title: Liquid-liquid extraction for aqueous organics via separatory funnel

11.0 Purpose/Applicability

This SOP is based upon EPA method 3510 in SW-846 series and describes a procedure for isolating organics from aqueous samples. This SOP was modified and developed specifically for the laboratory SPME calibration study contracted from USACE. The organics in this study include polycyclic aromatic hydrocarbons (PAHs) and Dibenzofuran (DBF)

12.0 Summary of Method

A measured volume of sample, here is 150 ml, is serially extracted with Methylene chloride using a separatory funnel. The extract is dried, concentrated, exchanged into acetonitrile for HPLC analysis

13.0 Interferences

Unwanted organic chemicals can be introduced into the sample extract through contaminated reagents, glassware, chemicals or through poor technique. Reagent and sample blanks are analyzed to insure that contaminants are not introduced into the sample extract.

14.0 Apparatus

14.1 250-ml seperatory funnel with Teflon stopcock

14.2 10 mm I.D. glass buret or Glass funnel as drying column

14.3 Nitrogen blow down system for concentrating extract

15.0 Reagents

HPLC grade Methylene chloride and Acetonitrile

16.0 procedure

16.1 ADD an accurately measured volume of sample to the separatory funnel.

16.2 Add 10ml of Methylene chloride to the separatory funnel, seal and shake the funnel vigorously for 1-2 minutes with periodic venting to release excess pressure

16.3 Allow the organic (bottom) layer to separate from the aqueous layer for a minimum of ten minutes. If an emulsion forms, attempt to disrupt it with stirring, centrifugation or filtration. Drain the organic layer into a 40ml brown sample vial to retain the aqueous phase in the seperatory funnel.

16.4 Repeat the extraction two additional times using fresh portions of solvent. Combine the three solvent extracts.

16.5 Dry the extract by passing it through a drying column or funnel containing sodium sulfate. Collect the dried extract in a sampling tube for nitrogen blow down.

16.6 Concentrate the extract to 2 ml and then solvent exchange into acetonitrile for HPLC analysis

17.0 Quality control

17.1 All quality control data should be maintained and available for easy reference or inspection

17.2 At least two sample blanks are analyzed to check the background PAH concentrations

17.3 Laboratory control samples are prepared by spiking site water at concentrations high enough to be detectable by direct injection on HPLC. Two LCS are analyzed before, in the middle and after the whole calibration study. The extraction efficiencies of each compound are calculated by comparing the concentration by liquid-liquid extraction and the concentration by direct injection by HPLC. This extraction efficiency is used to correct the measured aqueous concentrations of PAHs and DBF.

Reference

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 3510C. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.